

# A REDETERMINATION

— OF THE —

ATOMIC WEIGHT OF ZINC AND CADMIUM.

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DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES  
OF THE JOHNS HOPKINS UNIVERSITY FOR THE  
DEGREE OF DOCTOR OF PHILOSOPHY,

— BY —

HOWARD BELL ARBUCKLE.

1898.

Presses of Fenn & Owen, Petersburg, Va.





# A REDETERMINATION

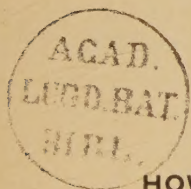
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## ACKNOWLEDGMENT.

THE AUTHOR feels deeply indebted to Professor Morse, under whose supervision this work was undertaken, for his constant advice and kindly interest.

He desires to express his sincere gratitude to Professor Remsen, Professor Howell and Dr. Andrews, whose instruction in Chemistry, Physiology and Biology, has been an essential part of his University course.

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## I.—INTRODUCTION AND HISTORICAL STATEMENT.

It would be eminently satisfactory to chemists if the standard methods employed in the atomic weight determinations of the elements could be brought into perfect agreement.

Every method has its imperfections, and we welcome the able experimenter who can show the author of the method not merely the imperfections, but how they can be corrected. There is left much to be done in atomic weight investigations of even the best known elements.

In his Stas Memorial address\* J. W. Mallet directs the attention of the chemist with enthusiasm to the many unsolved problems in this field now pressing their importance upon us.

Among the methods which have so long done service, none deserves more consideration than the Direct Oxide Method. That modification of this method, which employs the oxide derived from the nitrate by ignition, was introduced by Erdmann and Jacquelin, and has played an especially interesting role in investigations of zinc, cadmium and magnesium. The method was brought to its highest perfection in this laboratory, when Morse and Burton employed it in their work on the atomic weight of zinc.† So successful was its application to this problem that later Morse and Jones‡ used it to investigate cadmium, and Burton and Vorce|| magnesium. Not till within a few years were they called in question. T. W. Richards of Harvard University, in the course of his long and exhaustive investigation of the atomic weight of copper, fortunately hit upon a source of error in the oxide§ till then overlooked. He was able to prove that even at very high temperatures the

\*Chem. Soc. Proc., 1892, 203.

†Amer. Chem. J. 10, 311.

‡Amer. Chem. J. 14, 261.

||Amer. Chem. J. 12, 219.

§Proc. Amer. Acad., Arts and Sci., 26, 281.

oxide prepared from the nitrate retained gases, which could only be completely removed by solution in acids. So striking a phenomenon deserved further investigation. Accordingly, an examination of other oxides was begun by Richards and Rogers\* ending in 1893. Their paper establishes the fact that zinc oxide, magnesium oxide, and nickel oxide, derived from the nitrate, hold varying quantities of gases, even when ignited at white heat. The importance of this statement is at once apparent. It made necessary a revision of the work of Morse and Burton on zinc.

The phenomenon which Richards brought to light was not wholly unknown to chemists. In the literature, Erdmann and Marchand† in 1842 speak of copper oxide occluding, or condensing air; Frankland and Armstrong‡ in 1868 state that copper oxide derived from the nitrate contains nitrogen and carbon dioxide; Hilditch|| states that oxygen gas is occluded in copper oxide at red heat; Morley§ found that copper oxide gave off gas in a vacuum.

However, its importance was not realized until Richards showed the relation it sustained to atomic weight determinations. Inasmuch as it touches the work done in this University, and, more especially, because it would change the figures which Morse and Burton had determined for the atomic weight of zinc, it seemed advisable to repeat the determination of the atomic weight of zinc, making correction for the retained gases.

We proposed, therefore, to determine the atomic weight of zinc by means of the Morse-Burton method, so extended as to permit of a correct determination of the included gases.

The method used by Richards, which was well suited to his purpose and commendable for its simplicity and effectiveness, was not sufficiently refined for atomic weight work. Hence an entirely different plan for securing the gases was employed.

\*Proc. Amer. Acad., Arts and Sc., 28, 200.

†J. f. prakt. chem., XXVI, 461.

‡Chem. Soc. J. XXI, 89, 93.

||Chem. News, XLIX, 37, 1884.

§Am. J. Sci., XLI, 231, 1891.



A few words, by way of review of the work done on the atomic weight of zinc, may not be out of place before describing the method employed in this research. The following methods have been resorted to by the various experimenters in this field: 1. The oxide method, (*a*) the conversion of the metal into the nitrate, and then by ignition into the oxide (Gay Lussac, Berzelius, Jacquelin, Erdmann, Morse and Burton, (*b*) the conversion of the metal into the sulphate, then by ignition into the oxide (Jacquelin and Baubigny), (*c*) the conversion of the metal into the oxalate and then into the oxide (Favre), (*d*) the conversion of the lactate into the oxide (Pelouze); 2, the solution of the metal in acid and the combustion of the liberated hydrogen (Favre); 3, the ignition of the oxalate with the combustion of the carbon monoxide and the determination both of the oxide of zinc and of the carbon dioxide (Favre); 4, the solution of the metal in acid and the measurement of the hydrogen (Gay Lussac, Van der Plaats, and Reynolds and Ramsay); 5, the analysis of the double chloride of zinc and potassium, with a determination of the zinc and the chlorine (Marignac); 6, the determination of the electrical equivalent of zinc (Gladstone and Hibbert); 7, the analysis of zinc bromide and the determination of its relation to silver bromide (Richards and Rogers.) For a detailed historical statement of this work see the very complete account in the paper by Richards and Rogers\* on revision of atomic weight of zinc, and the sketch in the Morse-Burton† paper.

For convenient reference, the following summary of the results thus far obtained is presented:

|                                                           |        |
|-----------------------------------------------------------|--------|
| 1809. Gay Lussac, Mem d'Arceuil II 174 . . . . .          | 65. 55 |
| 1811. Berzelius, Pogg. Ann. VIII 184 . . . . .            | 65. 57 |
| 1842. Jacquelin, Ann. de Chim. et de Phys. [3] VII, 204 . | 66. 24 |
| 1844. Favre, Ann. de Chim. et de Phys. [3] X, 163 . . . . | 65. 99 |
| 1844. Erdmann, Berz. Jahres Bericht. XXIV, 132 . . . .    | 65. 05 |
| 1883. Pelouze and Fremy, Chim. Generale p. 55 . . . . .   | 65. 07 |
| 1883. Baubigny, Comptes Rendus, XCVII, 906 . . . . .      | 65. 41 |

\*Ztschr. Anorg. Chem. 10, 2.

†Amer. Chem. J. 10, 316.

|                                                               |                    |
|---------------------------------------------------------------|--------------------|
| 1883. Marignac, Archiv. Sci. Phys. et Nat. [3] X 5, 193 . . . | 65. 30             |
| 1885. Van der Plaats, Comptes Rendus c. 55 . . . . .          | 65. 34             |
| 1887. Reynolds and Ramsay, J. Ch. Soc. Trans. LI, 854 . . .   | 65. 67             |
| 1888. Morse and Burton, Amer. Chem. Jour. X, 311 . . .        | 65. 27             |
| 1889. Gladstone and Hibbert, J. Ch. Soc. Trans. LV, 443 . .   | 65. 44             |
| 1895. Richards and Rogers, Zeit. für Anorg. Ch. 10, 2 . . .   | { 65.459<br>65. 43 |
| 1895. Richards, Zeit. für Anorg. Ch. 10, 2 . . . . .          |                    |
| 1897. Morse and Arbuckle, Am. Chem. Jour. 20, 195 . . .       | 65.404             |
| 1897. Morse and Arbuckle, Am. Chem. Jour. 20, 195 . . .       | 65.456             |

The features which entitle the method of Morse and Burton to special consideration are 1, the purification of the zinc, 2, the use of porcelain crucibles, 3, the simplicity and accuracy of the plan of weighing. They were able to prove that in porcelain vessels the oxide of zinc did not dissociate or volatilize\* at the high temperatures of the muffle furnace and, furthermore, that there was no validity in Marignac's objection that "oxides of nitrogen remained undecomposed in the zinc oxide, though heated to a temperature at which it begins to dissociate."†

The simplicity of the method is highly commendable. It consists in converting the pure zinc into nitrate, the evaporation of excess nitric acid and partial decomposition of the nitrate in a hot-air bath, and, finally, the ignition of the oxide in the muffle furnace to constant weight.

## II.—PREPARATION OF THE OXIDE BY THE MORSE-BURTON METHOD.

### *Preparation of pure zinc.*

The metal employed in these experiments was a portion of the sample used by Burton and was prepared by fractional distillation in a vacuum. For full particulars see the paper.‡ In brief, the plan was as follows: 200 grams of the purest zinc obtainable are placed near the closed end of a hard glass combustion tube which has been divided into three compartments by depressing the softened tube at two points by means of a red-hot file. The tube was exhausted

\*Amer. Chem. J. 10, 325.

†Amer. Chem. J. 10, 326.

‡Amer. Chem. J. 10, 312.

and then heated in the furnace. Only the material collected in the middle compartment was preserved for further treatment and this was four times redistilled. The metal so prepared was examined spectroscopically by Prof. Ames of this University, and pronounced free from calcium, arsenic, lead, cadmium, tin, and indium, lines of which were found in samples of so-called C. P. zinc. His report may be seen in the Morse-Burton paper.

*Preparation of pure Nitric Acid.*

A platinum retort could not be used for distillation of the acid, as the gold in the soldered joints is a source of impurity, so the acid was distilled from a glass flask against a large platinum dish, underneath which and separated from which by small platinum hooks, was placed a much smaller platinum dish to serve as a receiver. The larger platinum dish was suspended by platinum wires from a glass support. The acid used, the purest obtainable, was slightly diluted with specially prepared water and treated with silver nitrate. The distillation was carried out in a room removed from the fumes and impurities of the laboratory and every possible precaution was taken against dust. The distillation was conducted very slowly, and the mouth of the distilling flask was never allowed to come in contact with the platinum. The acid was distilled five times and was kept, in the open platinum dish used as receiver, under a bell-jar which was in a dark place. The acid was transferred from this platinum dish to the crucibles by means of a platinum spoon. All the platinum ware used in this work was treated for several hours at red heat with vapors of ammonium chloride to remove iron.

On evaporation of considerable quantities of this pure acid on platinum no distinctly visible residue was formed, but the microscope revealed a yellowish marking, doubtless due to evaporation in the air, which Stas asserts will always attend evaporation under these circumstances. This very



slight residue was shown not to amount to weighable quantities in evaporation of twice the amount of acid used in any of our experiments.

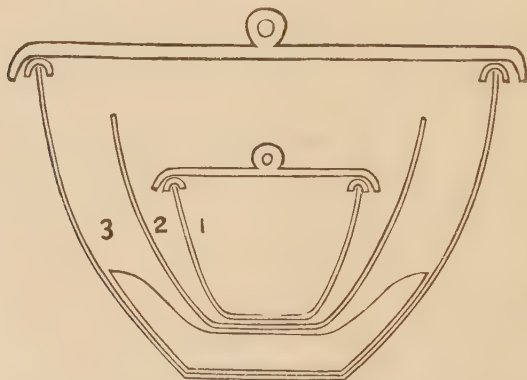
*Purification of Water.*

Distilled water was treated with acid bichromate of potassium and twice distilled through alkaline permanganate, and condensed in a tin tube. The water thus obtained was twice distilled against a platinum dish and condensed in a platinum receiver.

*The Arrangement and Preparation of the Crucibles.*

The glaze was removed from the lids of the crucibles and from the lower half of the outer portion of crucible 2 in figure 1. This was done with hydrofluoric acid, great care being exercised to remove all of the white pulverulent deposit which is left more or less firmly entangled in the biscuit. We found that this was greatly facilitated by immersing the crucible the moment it is removed from the hydrofluoric acid bath, in hot concentrated sulphuric acid and afterward in boiling water. Figure 1 shows the arrangement of the crucibles: 1 is a small crucible (00) in which

*Fig. 1.*



the zinc is dissolved, and the oxide prepared. Its lid is separated by small platinum hooks from the edge of the

crucible. 2 is a larger crucible (II) without lid, which rests on a scorifier placed in the bottom of 3, a still larger crucible (IV) with lid also separated from edge of crucible by platinum hooks.

*Mode of Procedure.*

After the pair of crucibles in which the oxide is to be prepared is gotten ready, a precisely similar pair to be used as a tare is brought to within a milligram of the same weight by adding pieces of porcelain. The platinum hooks have been previously adjusted with a file, so that the difference in weight between those belonging to the pair of crucibles to be weighed and to the tare does not exceed one-tenth of a milligram. The pairs are now transferred to the large crucibles 3, figure 1, whose lids must also be separated by platinum hooks, and heated in the muffle. Now the pairs are well brushed with a camel's hair brush and more accurately adjusted, so that the difference in weight is only a small fraction of a milligram. Again they are heated and the difference in weight accurately determined. Three times the empty crucibles are heated and weighed. In no case did the total difference between the weighings exceed one-fiftieth of milligram, while in one instance (Pair IV) the agreement was phenomenal, the difference not being detectable.

Next in order was securing the piece of zinc. The bar of zinc was placed on an anvil covered with several thicknesses of filter paper which had been extracted with absolute ether. A clean, sharp cold chisel was placed on the zinc and struck a smart blow. The bar of zinc was then wrapped in filter paper and the piece, weighing about one gram, broken off with a pair of tongs. A hard file, washed in absolute ether, was used to remove the outer surface of the zinc, which had been in contact with the glass. This piece was placed in crucible 1, figure 1, and carefully weighed three times. Into the crucible was now introduced one cubic centimeter of water with a small pipette pre-

pared for the purpose, and small quantities of the pure nitric acid were added with the platinum spoon, using the greatest care, until the solution was well-started. After one hour, more nitric acid was added, the crucible being only partially uncovered for a moment, and the solution completed by very gently warming in an air-sand-bath, consisting of a deep iron dish half filled with sand into which was fitted a circular asbestos board carrying a No. IV porcelain crucible fastened tightly in a circular aperture cut in the centre of the asbestos disk. The asbestos cover prevents dust from the sand getting into the crucibles. In this same bath the excess of nitric acid was evaporated, and by very gradually raising the temperature the nitrate was in large measure changed to the oxide. This careful operation required about ten hours. With extreme care only the merest traces of the material will be transferred during the heating to crucible 2, figure 1, or to the lid and outer side of crucible 1. The final heating in the air bath was with a triple burner for three hours. The tare received the same amount of water and acid and was subjected to precisely the same treatment as the pair in which the zinc was converted to oxide, which for convenience we may designate as the "oxide pair." The pairs were then placed in the larger crucibles and transferred to the muffles, where they were heated for four hours and a half to a temperature which melted the tip broken from a file and placed on a scorifier beside the crucibles. In this heating we took as much pains as possible to keep the conditions similar for the various experiments. The coke was measured and the arrangement of draughts always the same. At the temperature obtained the glaze on the crucibles was melted, and in one experiment a crucible which was overturned was taken out a shapeless mass, showing that it was softened. It was found that there was no appreciable change in weight after the first heating. The total apparent difference in weighings, after three heatings, rarely



exceeded one-fiftieth of a milligram, and was often much less. The oxide thus prepared is beautifully crystalline, and, with two exceptions, perfectly white when cold.

### III—THE WEIGHING.

#### *The Balance.*

The Balance employed is a long-arm balance constructed by Becker and Sons, and has been used at this University only for such work. It is capable of adjustment to a sensibility of twelve divisions for one milligram weight. This instrument was used by Morse and Burton in their investigation of the atomic weight of zinc, and if, as appears to be the case, it has never been readjusted, it has improved in sensibility in the years which have elapsed. Burton found a sensibility of 5.05 divisions for one milligram, with a load of twenty-five grams. The sensibility is now 5.55 divisions with that load.

#### *The Weights.*

The weights were specially adjusted by Becker of New York and afterwards examined and their relative values accurately determined. Before undertaking this work the weights were examined and were found in good adjustment still.

#### *Balance-room.*

A new underground balance-room has been fitted up by the University which has offered unusual opportunities for such work. This room has no heating apparatus in the room itself, but is heated through the walls and has no direct communication with the outside, its one door opening into another room, which is in the basement of McCoy Hall, under which the balance-room is located. In the centre of the room is a cloth tent well covered with paper, in which the balance is situated on a very heavy three-legged table, the table being weighted down with a large marble slab. The legs of the

table are in boxes of saw-dust; the legs of the balance are on blocks of rubber an inch thick. The great advantages of the balance-room are, 1, the uniformity of temperature; 2, the freedom from the effect of surface vibrations, which in a city is a constant source of annoyance; 3, the freedom from the swing and jar of the building. Two electric lights, placed above and back of the operator's head, furnish the light.

*The Method of Weighing.*

Notwithstanding the favorable conditions attendant upon the new balance-room, it was found best to do all the weighing between the hours of eleven and five at night, as the travel on the streets passing the University practically ceases during these hours. In the balance-room is placed a closed vessel of mercury which very perfectly indicates the slightest tremor that affects the balance. So well is the balance mounted that the walking of the operator in the tent does not cause a perceptible effect on the mercury-mirror.

Before beginning a weighing, the operator took his seat immediately before the balance and waited until the thermometer, hanging just over the balance case, indicated constant temperature. This required about one hour. The lights and the presence of the operator raised the temperature about two degrees, and often, for eight hours afterwards, the change of temperature did not amount to one-half a degree. The zero point of the empty balance was then three times determined. The crucibles were placed on the pans and again the zero point three times determined. The sensibility was determined, then the loads were removed and the zero point of the empty balance again determined. The crucibles were then returned to the pans, exchanging sides, and the zero point thrice determined; the sensibility was again determined, and after removal of load, the zero point of the empty balance ascertained the third time. Six vibrations to one side and five to the other were employed in the zero point deter-

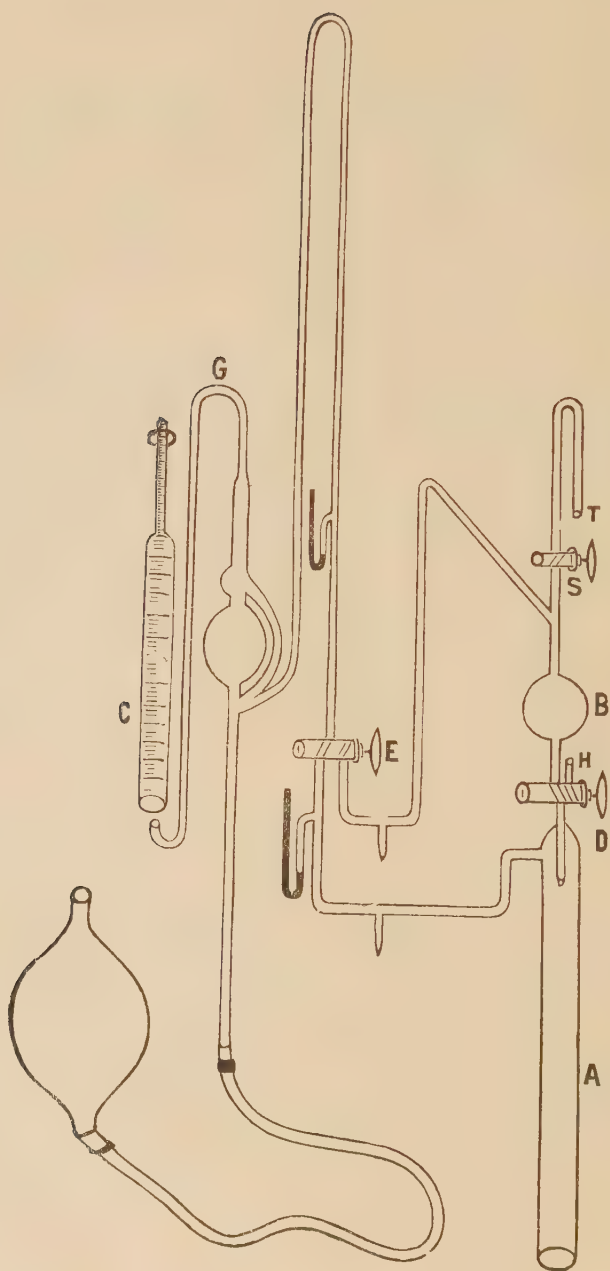
minations. When the zinc or oxide was in the "oxide pair" the same plan was followed, after adding the requisite weights to the pans carrying the tare. In general, the number of weighings were: empty crucibles three times, with zinc twice, with oxide three times, weighing in both pans each time, determining sensibility each time, and obtaining zero point of empty balance before and after each weighing. From the above statement it is seen that two very common errors are overcome by the method adopted: 1, the difference of arm length, overcome by the method of Gauss; 2, the condensation of moisture on the vessels employed, overcome by use of tares. It may be stated that, before weighing, the crucibles were removed from the desiccators and allowed to remain in the balance case a half-hour. A very striking illustration of the value of tares in weighing is to be had in the fact that, if the crucibles containing the zinc oxide were weighed five minutes after removing from desiccators and again thirty minutes later, there was a slight increase in weight amounting sometimes to one-twenty-fifth of a milligram, indicating that the condensation of moisture is greater on the zinc oxide than on the weights counterbalancing it.

#### IV.—DETERMINATION OF THE GASES HELD IN THE OXIDE.

##### *Apparatus for Abstracting the Gases.*

The form of apparatus which enables us to test every trace of oxide employed in each experiment for gases retained is seen in the accompanying figure. It may be said to consist of four parts, a mercury air pump, a bulb "b" in which the acid was exhausted, a tube "a" of such diameter that the pair of crucibles containing the oxide, just as weighed, could pass up the tube as it was exhausted, and of such length that the crucibles were brought within an inch of the end of the small tube which passes down into





"a" from above, when the tube is thoroughly exhausted, and, finally, the eudiometer "c" of special construction.

The apparatus is entirely of glass, no rubber connections, the tube connecting the mercury reservoir with the pump excepted, of course. The bulbs, the tube "a," and the stop cocks were made in New York, but the apparatus was put together in the laboratory.

Mr. E. W. Magruder deserves especial mention here for giving us so much of his time and the benefit of his skill in glass blowing.

The whole apparatus was mounted on wood, the wooden "keepers" being placed parallel to the grain of the cross-pieces to which they were fastened. The cross-pieces were so placed that the grain was at right angles to that of the long board serving as support. This is very necessary to prevent the straining of the various parts through the expansion and contraction of the wood in consequence of the varying humidity of the air. The stop cocks were surrounded by mercury troughs made of wood. These were made by boring holes of proper size half way through blocks of wood and then splitting the blocks into halves, cutting passage ways for the tube or tubes below stop-cocks. These halves were brought into position and drawn together by screws, being made mercury tight by using a soft gum and bees' wax. The support for the mercury troughs was independent of the apparatus. The trough surrounding stopcock "d" was on a support that moved up and down with the tube "a," (this, as we will see, was not perfectly stationary), thus bringing no strain on the delicate apparatus.

Before putting mercury into these troughs, the stop-cocks, connecting tubes and the sides and bottom of the troughs were washed well with mercuric chloride. The mercury reservoir, which served to hold the mercury at the open end of tube "a," was a tall glass cylinder. At the bottom of this was placed a thick disk of rubber packing

with a large aperture cut in the centre which communicated with the margin by deep grooves cut in the rubber. The reservoir, when brought up to the open end of tube "a" with the rubber disk in place, had a small table slipped under it, which was provided with leveling screws, by means of which the reservoir could be brought tight against the tube "a." The mercury was passed into the reservoir by an equal-armed siphon which passes the mercury into the reservoir and out. When it became necessary to get rid of the vacuum in "a," the air was allowed to enter at "h" by means of the two-way stop cock.

To introduce the acid into "b," the bulb is exhausted, the outlet "t" immersed in the acid, and the stopcock "s" cautiously opened. The acid passes into the bulb, giving up at once most of the gases held in solution.

#### *Solution of the Oxide.*

The only sure way of securing all the gases held in the oxide was found to be by dissolving it in acid in a vacuum. Sulphuric acid is the only acid that can be used with convenience. The form of apparatus requires that the solution should take place in the cold. At once a difficulty presented itself.

The oxide of zinc, especially the pure oxide, is very difficultly soluble in cold sulphuric acid. Considerable experimenting showed that in very dilute and also in very strong sulphuric acid the solution could not be effected without heat, but most fortunately it was found that an acid of particular strength would dissolve the oxide in the cold. The acid actually used showed on titration 364.9 grams to 1 litre. The limits, too, are very narrow, certainly not over two per cent. It generally required ten hours to effect the complete solution of a specimen of the oxide; in one case, however, only four hours seemed necessary. After thorough exhaustion samples of the acid were removed and titrated and the strength had changed to 373.4 grams in the litre.

So the acid actually employed in dissolving the oxide was slightly stronger than that mentioned above.

*Mode of Procedure.*

The efficiency and accuracy of the apparatus was first tested by a series of blank experiments in which the tare crucibles replaced the "oxide pair." The first blank served to remove the air which remained in the channel of the stopcock "d," this being filled with exhausted acid during all subsequent determinations. When the apparatus was shown to be in perfect order, the testing of the oxide began.

The crucible pair containing the weighed oxide of experiment No. 1, was placed in a crystallizing dish of proper size, the lid of the inner crucible was transferred to crucible 2, so as to insure the bringing of every trace of oxide into the vacuum. File marks were made in every direction across the bottom of the crystallizing dish to provide for the escape of air which otherwise might be caught and held between the mercury and glass. The crystallizing dish containing the crucibles was placed on the rubber disk at the bottom of the cylindrical mercury reservoir, and the reservoir was brought up underneath the open end of tube "a," the leveling table slipped underneath this for a support, and by means of the screws the table was carefully raised until the tube, "a," was pressing firmly and evenly on the rubber disk. This was necessary, because when the tube is exhausted the pressure of the atmosphere, tending to force the tube down, is considerable. It is this change in pressure that causes the whole apparatus to move down during exhaustion and to move up when the vacuum is relieved. This fact calls for great care in manipulating the apparatus to avoid breakage. The mercury was allowed to flow into the reservoir by opening the pinch-cock in the middle of the equal-armed siphon, and then exhaustion was begun.

If it is necessary after exhaustion to raise the crucibles



nearer the small tube which admits the acid, it is easily and accurately done by bringing more mercury into the reservoir. This was never done, however, until we were ready to introduce the acid.

The last stages of the exhaustion are slow and tedious, and it was carried on at intervals for twenty-four hours, until the last traces of air were gotten over. The progress of the final exhaustion was watched by means of the McCloud gauge, which is formed in the curved portion of the tube "g"; the vibration of the column of mercury in "g" was a very delicate test of the pressure existing in the pump, 400 cc. being compressed into  $\frac{1}{2}$  cc. The acid bulb was simultaneously exhausted, and just as rigid tests were applied to it as to the tube "a." When the tube "a" had been thoroughly exhausted by occasional pumping for twenty-four hours, the oxide was allowed to stand in the vacuum for twelve hours, being shut off from the pump by stopcock "e". It was then tested to see if any gas could be delivered in the eudiometer; in every case the result was negative. The crucibles were now brought up close to the tube which admits the acid, and by means of the stopcock "d" the acid was allowed to flow quickly into the crucibles until the inner crucible was completely submerged. Almost instantly the solution began, and the evolution of gas was strikingly apparent through the expanded bubbles produced in the solution by the low pressure in the apparatus. After ten hours the gas liberated was pumped out and delivered into the eudiometer "c". The crucibles were, however, allowed to remain in the vacuum twenty-four hours longer, but in no case was any appreciable amount of gas liberated after the first ten hours. The eudiometer was now removed to the gas analysis room, and the gas carefully measured and analyzed.

#### V.—MEASURING THE GASES.

The gases were collected in a eudiometer "c" (figure 2) of special form, the upper portion of which was so narrow

that a millimeter division was equivalent to only 0.03 cc. This eudiometer was calibrated with the greatest care. Before filling it with mercury, the upper portions were wiped out with moistened paper to insure the measuring of the gases saturated with water vapor.

The eudiometer containing the gases was transferred to the gas analysis room and every precaution taken in measuring the gases. Two carefully adjusted thermometers were employed to ascertain the temperature. These instruments were graduated to tenths of a degree. Two barometers of different construction were used. All these readings were taken with a telescope at different times during the day, the operator entering the room only for a minute at these times.

## VI.—ANALYSIS OF THE GASES.

### *Mode of Procedure.*

A few preliminary samples of these gases were tested for carbon dioxide with absolutely negative results. In the regular determinations, in which we had every reason to believe, we would likewise find no carbon dioxide, we thought best to determine the oxygen and allow the spectroscopist to pronounce judgment on the residue. In such small volumes of gas, the method which most commends itself to us is the explosion with electrolytic hydrogen. The method of procedure finally adopted was the following: 1. Into the accurately measured gases a small quantity of electrolytic gas was introduced and exploded and final readings were not taken for six hours. In each experiment the volume agreed with the original volume within the limit of necessary error. 2. Small quantities of hydrogen were introduced, observing the usual precautions, and the mixtures were repeatedly exploded until no further diminution of volume resulted. 3. A small quantity of hydrogen was added and then the proper amount of electrolytic gas. This mixture was exploded. 4. Finally electrolytic gas was added

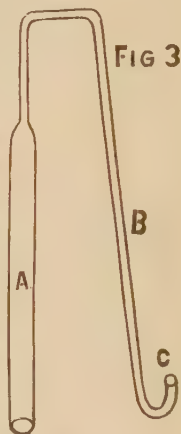
and exploded. The precautions mentioned above under "measurement of gases" were observed here at each step. This furnishes the data for determining the oxygen present.

The electrolytic gas was furnished by the Bunsen apparatus and was tested each time by exploding it by itself and with air repeatedly. The electrolytic hydrogen was prepared with the apparatus devised by Magruder,\* which, it may be of interest to state, was suggested by a study of the faults of the Bunsen apparatus in its bearing on this work.

*Apparatus for Keeping Residual Gases.*

The accompanying figure shows the apparatus which was found convenient for keeping the residual gases for spectroscopic examination:

This is placed upright in a mercury trough and filled with mercury by partial exhaustion. Until the gases are introduced it is kept full of mercury by clamping a rubber tube attached at "c." After the first sample of residual gases is introduced, the rubber tubing may be removed and the gases are then held between the columns of mercury in "a" and "b". The introduction of the gas is simple. The apparatus is moved to a shelf



at one end of a long mercury trough, the open end of the tube "a", which is considerably larger than the open end of the eudiometer, being brought over a slit in the shelf, which serves as a guide for the end of the eudiometer under the mercury. The eudiometer is brought carefully into proper relation to the tube, and then lowered to a horizontal position. The residual gases are thus transferred completely to the gas holder after each analysis.

For the purpose of delivering these gases, the mercury trough was provided with a deep well into which the tube

\*Amer. Chem. J. 19, 811.

“a” could be sunk. By gently warming the tube “b” the mercury could be brought into “b” below the level of the mercury in the trough when, the apparatus acting as a siphon, the last traces of the gases are swept out by the mercury.

To make such a mercury trough, a large block of soft wood was selected, and after cutting out the trough to proper depth, the well was made by boring a hole in the bottom.

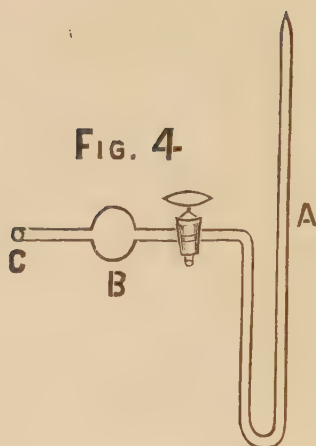
*Spectroscopic Examination of the Residual Gases.*

In order to apply an accurate correction to the atomic weight, it was necessary to determine what gases remained after the determination and removal of oxygen.

In the residual gases were large quantities of hydrogen. It was deemed most satisfactory to remove this hydrogen and submit the residue to a strict spectroscopic examination, for which there are unusual facilities in the Physical Laboratory. Accordingly, the gases were transferred to the eudiometer as described, and the hydrogen was removed by exploding with oxygen, obtained by reversing the current in the Magruder apparatus. This apparatus gave oxygen containing less than one per cent. of hydrogen.

The sparking tubes were exhausted for three days, and sparked from time to time. Although we had every evidence of the absence of air, there remained slight traces of hydrogen, explained by the fact that these tubes had been used for the examination of hydrogen, and the platinum electrodes could not be easily freed from the last traces of this gas. As small quantities of hydrogen were not objectionable, the gases were now introduced. A convenient device for doing this is shown in the figure.





The tube "a" is drawn out to a very small point and is of such length that when introduced into the eudiometer the tip reaches close to the top. This tube was filled carefully with mercury up to the stopcock and then introduced into the eudiometer containing the gases. The tube was then sealed at "c" to a tube communicating with the air pump. The stopcock was tested for three days. When all parts of the apparatus, including the channel of the stopcock, were thoroughly exhausted, very carefully the stopcock was turned and the mercury passed through into the bulb "b", the gases passing into the sparking tubes. When the proper pressure was indicated, the sparking tubes were sealed off and handed to Prof. Ames, of the Physical Laboratory. Dr. Randall, of the Chemical Laboratory, rendered most important service in preparing the sparking tubes. His experience in such work made his advice and assistance especially valuable, and we are much indebted to him for the use of his apparatus and for his personal aid.

Prof. J. S. Ames and Dr. W. J. Humphreys made a thorough examination of the gases, and in their report assert that they found, besides the oxygen and slight traces

of hydrogen known to be present, only nitrogen. This enables us to state that the gases obtained from our pure zinc oxide consist of oxygen and nitrogen only in varying proportions. See tabulated results.

#### VII.—TEST FOR NITRIDES.

That some nitrogen might be retained in the form of nitride hardly seemed probable, but the mere possibility of such a phenomenon led us to put the question to an accurate test. The acid which had been employed in the solution of the several samples of oxide was preserved. The quantity of the acid was ascertained by weighing, and by determining the specific gravity, and the sulphuric acid was determined in measured portions by precipitating with barium chloride. The strength thus being determined, volumes of this equivalent to ten cc. volumes of the original acid were submitted to the Nessler test for ammonia. No appreciable increase in the ammonia found in the original acid was noticed. The results are very conclusive. In three experiments, ten cc. of the original acid gave 0.01 mg.; 0.012 mg.; 0.01 mg. of ammonia; equivalent volumes of the acid used gave 0.012 mg.; 0.012 mg.; 0.013 mg. of ammonia.

We are, therefore, justified in asserting that our oxides were free from nitrides.

#### VIII.—RESULTS.

Below are given the results of the eight experiments that were carried out after our apparatus and methods had assumed their final satisfactory form:

The weights are corrected for air displacement. The gas volumes are given at 0° and 760 mm., and we assume the true weights of oxygen and nitrogen to be 1.42923 g. and 1.2546 g. respectively, which are the generally accepted weights of a litre of these gases at standard conditions, latitude 45°, sea level. The error involved in this assump-

tion for Baltimore is too small to deserve notice—In the calculations the atomic weight of oxygen is assumed to be 16.

## SUMMARY OF RESULTS.

| Number of Sample. | Weight of Zinc. | Weight of Oxide. | Uncorrected Atomic Weight. | Gas Volume 0°, 760mm. | Percentage of Oxygen. | Corrected Atomic Weight |
|-------------------|-----------------|------------------|----------------------------|-----------------------|-----------------------|-------------------------|
| I                 | 1.19573         | 1.48860          | 65.324                     | .468 cc.              | 26.28%                | 65.459                  |
| II                | 1.03381         | 1.28707          | 65.312                     | .402 cc.              | 18.14%                | 65.445                  |
| III               | 1.06519         | 1.32599          | 65.349                     | .342 cc.              | 18.42%                | 65.459                  |
| IV                | 1.05802         | 1.31711          | 65.338                     | .312 cc.              | 18.58%                | 65.440                  |
| V                 | 1.26618         | 1.57619          | 65.348                     | .521 cc.              | 13.82%                | 65.489                  |
| VI                | 1.03783         | 1.29198          | 65.336                     | .408 cc.              | 35.28%                | 65.475                  |
| VII               | 1.08655         | 1.35276          | 65.307                     | .412 cc.              | 19.55%                | 65.437                  |
| VIII              | 1.11363         | 1.38647          | 65.307                     | .456 cc.              | 18.62%                | 65.447                  |

Average=65.328  
Total Difference=.042

Average=65.456  
Total Difference=.052

## BLANK EXPERIMENTS.

|     |                                                  |
|-----|--------------------------------------------------|
| I   | a trace.                                         |
| II  | 0 cc.                                            |
| III | 1 mm=(less than 0.01 cc. at standard conditions. |

## IX—REMARKS.

The atomic weight calculated from the weights of the oxide, without correction for the gas contained, is 65.33. This is higher than the results of Morse and Burton by nearly 0.06. Since Richards and Rogers found that the quantity of gas retained diminished with the increase of temperature, we are led to believe that our oxide was subjected to a higher temperature than that of the former series. Though we endeavored to maintain the same conditions under which the former work was done, a difference in temperature may be explained by the fact that we were compelled to use another furnace, which seemed to be more efficient, or the quality of the fuel may have been better.

The difference, 0.06, corresponds to 0.14 cc. of gas per gram of oxide, so that the oxide of Morse and Burton must

have retained 0.14 cc. of gas per gram of oxide more than ours, probably because of the lower temperature to which it was heated.

An examination of the results reveals the fact that the oxygen and nitrogen are present in varying proportions.

Considering this fact and the conditions under which the oxide was prepared and the temperatures to which it was heated, as well as the interesting variation in volume of the gases at different temperatures which was shown by Richards, we are forced to adopt as the most satisfactory view that already suggested, that the oxygen and nitrogen arise from the  $\text{NO}_3$  group and are retained, pent up, as it were, in the oxide, owing to certain physical and mechanical causes. There are certain facts, however, which do not accord fully with this view. The gases are not given up in a vacuum, though the oxide was kept in a vacuous space for two days. It is clearly not to be compared with the so-called occlusion of gases by metals. In fine, it is very difficult to explain why these gases are not given up in a vacuum, if their retention be due to physical causes alone. If the oxide had, at the high temperatures employed, reached a state of fusion, we might imagine the gases arising from the  $\text{NO}_3$  group, first held in solution and then, on the cooling of the oxide, encysted in minute particles of the oxide. Gases thus retained might be given off only on complete solution of the oxide.

We know absolutely nothing about the fusion of zinc oxide and, therefore, can adduce no evidence for the above suggestion. On the other hand, there are no facts in our possession which point to chemical combination. Further investigation may lead to very interesting but entirely new ideas.

In the following table is given the volume of gas per gram of oxide for the individual determinations. It is worthy of mention that the volumes of oxygen and nitrogen



taken together are much more nearly constant than the quantities of either of the gases.

|               |                |               |                 |
|---------------|----------------|---------------|-----------------|
| I. 0.314 cc.  | III. 0.258 cc. | V. 0.329 cc.  | VII. 0.305 cc.  |
| II. 0.312 cc. | IV. 0.237 cc.  | VI. 0.315 cc. | VIII. 0.329 cc. |

#### X. RICHARDS' METHOD AND RESULTS.

It may be of interest to give a brief comparison of our results with those of Richards and Rogers. It will be remembered that they did not dissolve their oxides in a vacuum, but in the bulb of a bent tube closed at one end, the air being removed by filling with water and boiling, the oxide and acid being introduced afterwards. The gas was collected in the graduated closed limb. They also employed flasks into the stoppers of which concentric funnels were fitted. The gas passed off through a delivery tube. Their paper should be consulted for details. Their method is subject to some errors that exclude it from atomic weight work; it was, nevertheless, very efficient and commendable for simplicity, and it is very interesting to notice how well we corroborate their results, provided we select those experiments whose conditions were most similar to ours. These were few. Below are a few of their results, and placed by their side those of ours which are comparable, considering the fact that their gas volumes are not brought to strictly standard conditions,  $22^{\circ}.760$  m.m. being approximately the temperature and pressure.

| RICHARDS' AND ROGERS' RESULTS. |                |                             |                                                                         | RESULTS OF THIS PAPER. |                |                             |                                                                     |
|--------------------------------|----------------|-----------------------------|-------------------------------------------------------------------------|------------------------|----------------|-----------------------------|---------------------------------------------------------------------|
| Weight of Oxide.               | Vol'me of Gas. | Volume of Gas for 10 Grams. | Analysis.                                                               | Weight of Oxide.       | Volume of Gas. | Volume of Gas for 10 Grams. | Analysis.                                                           |
| 1.07                           | .42 cc.        | 3.9 cc.                     | $\text{CO}_2 = 0.0\%$<br>$\text{O}_2 = 16.9\%$<br>$\text{N}_2 = 83.1\%$ | 1.317                  | .525 cc.       | 3.98 cc.                    | $\text{CO}_2 = 0$<br>$\text{O}_2 = 18.58$<br>$\text{N}_2 = 81.42$   |
| 1.125                          | .48 cc.        | 4.3 cc.                     |                                                                         |                        |                |                             |                                                                     |
| .72                            | .33 cc.        | 4.6 cc.                     |                                                                         |                        |                |                             |                                                                     |
| 1.0125                         | .45 cc.        | 4.4 cc.                     | $\text{CO}_2 = 0.0\%$<br>$\text{O}_2 = 24\%$<br>$\text{N}_2 = 76\%$     | 1.326                  | .57 cc.        | 4.3 cc.                     | $\text{CO}_2 = 0.0$<br>$\text{O}_2 = 18.42$<br>$\text{N}_2 = 81.58$ |

In Richards' work at highest temperatures, the percentage of oxygen varied from 16.9 % to 24 %. In our work the variation was from 13.82 % to 35.28 %, but the average is almost identical.

As a good representative of the experiments which Richards and Rogers carried out at much lower temperature, we choose one in which the blast lamp was used. It is enough to show the great difference which the increase of temperature makes.

| Weight of Oxide. | Volume of Gas. | Volume of Gas<br>per 10 Grams. | Analysis.                                                               |
|------------------|----------------|--------------------------------|-------------------------------------------------------------------------|
| 1.02 g.          | 1.52 cc.       | 14.9 cc.                       | CO <sub>2</sub> = 1.3<br>O <sub>2</sub> = 53.1<br>N <sub>2</sub> = 44.8 |

In our work the gas volumes would be expected to be smaller, as the whole oxide is subjected to solution and the portions next to the porcelain were converted to an appreciable extent into silicate, yet the results are almost identical. Richards tested samples taken from larger lots of oxide which he had prepared.

#### XI.—THE ATOMIC WEIGHT OF ZINC.

As regards the final corrected result, 65.456, it is practically identical with the number 65.459 which was obtained by Richards and Rogers in one series by the bromide method, and not very different from 65.43 obtained by the same experimenters later, but it differs from the later result, 65.404 of Richards himself by 0.053. It is in fair agreement also with the results of Baubigny by the sulphate method, 65.41, which, notwithstanding the error which has been pointed out, an error which in all probability was very small, must be placed among the more refined determinations. If this error could be corrected, the figure would be larger and so possibly nearer our own.

Finally, the more recent work of Gladstone and Hibbert by determination of the electrical equivalents of zinc presents 65.44 as the figure. For four distinct methods, therefore, we have the exceedingly small range, from 65.404 to

65.456, a fact which places the atomic weight of zinc among the most certain.

## PART II.—ATOMIC WEIGHT OF CADMIUM.

### I.—INTRODUCTION AND HISTORICAL STATEMENT.

There has been a puzzling discrepancy in the results of the atomic weight determinations of cadmium for many years, and recent work has not thrown very convincing light on the problem.

The figures obtained by the various experimenters may be divided into two sets. The first set varies between the limits 111.610 and 112.15, omitting Stromeyer's figure, which has only historical interest, and the second set varies between 112.239 and 112.476. The first series includes thirteen results, of which six were based on the weight of the oxide, four on the weight of the sulphide, and three on the electrolysis of cadmium salts. The average of these is 111.95.

The second series includes four results, two derived from the relation of the bromide to silver, and two from the relation of the chloride to silver. The average of these is 112.32.

Many of the figures thus far obtained have been considered only approximations, as the difference in individual experiments amounts sometimes to one unit, and in several cases to two-tenths of a unit. One would be inclined to give more weight to the first series, because three distinct methods gave closely agreeing results. Selecting the results of Lenssen, Morse and Jones, Lorimer and Smith, and Hardin, we find that three distinct methods gave results closely agreeing with the above stated average, 111.95.

On the other hand the higher results are derived from practically one method, the "halogen method," and these results by different experimenters do not agree so well. The tendency has been to accept the lower figures.

In this first series the results obtained by Morse and

Jones by converting the nitrate into the oxide, had from the first been looked on with favor, and when Richards and Rogers in their paper\* on the "Occlusion of Gases by Metallic Oxides," stated that gases were not occluded in cadmium oxide, this work was left on a still firmer basis. Notwithstanding Bucher's statement† that the oxide prepared from the nitrate was heavier than the oxide he had converted into the nitrate, a fact he did not explain, the figure 112.07 obtained by Morse and Jones seemed to be accepted as very close to the truth.

Having corroborated the statements of Richards and Rogers with regard to the gases retained in zinc oxide, we thought it important to examine cadmium oxide in the same way, as a confirmation of the statements of Richards and Rogers about this oxide would be very valuable evidence of the reliability of the oxide method, as applied to cadmium.

Before passing to a consideration of the method, we give a chronological summary of the results which have been obtained for the atomic weight of cadmium:

|                                                |                                                             |          |
|------------------------------------------------|-------------------------------------------------------------|----------|
| 1818. Stromeyer . . . . .                      | Cd: Cd O . . . . .                                          | 111.483  |
| (Schweigger's Jour. 22, 336.)                  |                                                             |          |
| 1857. Von Hauer . . . . .                      | Cd S O <sub>4</sub> : Cd S . . . . .                        | 111.935  |
| (Jour. f. prakt. Chem. 72, 338.)               |                                                             |          |
| 1859. Dumas . . . . . 1st series . . . . .     | Cd Cl <sub>2</sub> : Ag . . . . .                           | 112.476  |
| (Ann. Chim. Phys. [3], 55, 158)                |                                                             |          |
|                                                | 2d series Cd Cl <sub>2</sub> : Ag . . . . .                 | 112.007  |
| 1860. Lenssen . . . . .                        | Cd C <sub>2</sub> O <sub>4</sub> : Cd O . . . . .           | 112.043  |
| (Jour. f. prakt. Chem. 79, 281.)               |                                                             |          |
| 1882. Huntington and Cooke . . . . .           | Cd Br <sub>2</sub> : Ag. Br . . . . .                       | 112.239  |
| (Proc. Amer. Acad. 17, 28.)                    |                                                             |          |
|                                                | Cd Br <sub>2</sub> : Ag . . . . .                           | 112.245  |
| 1890. Partridge . . . . . 1st series . . . . . | Cd C <sub>2</sub> O <sub>4</sub> : Cd O . . . . .           | 111.816  |
| (Amer. Jour Sci. [3], 40, 377)                 |                                                             |          |
|                                                | 2d series Cd S O <sub>4</sub> : Cd S . . . . .              | 111.727  |
|                                                | 3d series Cd C <sub>2</sub> O <sub>4</sub> : Cd S . . . . . | 111.610  |
| 1892. Morse and Jones . . . . .                | Cd : Cd O . . . . .                                         | 112.0706 |
| (Amer. Chem. Jour. 14, 261.)                   |                                                             |          |
|                                                | Cd C <sub>2</sub> O <sub>4</sub> : Cd O . . . . .           | 112.032  |
| 1892. Lorimer and Smith . . . . .              | Cd O : Cd . . . . .                                         | 112.055  |
| (Zeit. f. anorg. Chem. 1, 364.)                |                                                             |          |
| 1894. Bucher . . . . .                         | Cd C <sub>2</sub> O <sub>4</sub> : Cd O . . . . .           | 111.89   |
| (Doctoral Dis. J. H. Univ 1894.)               |                                                             |          |
|                                                | Cd C <sub>2</sub> O <sub>4</sub> : Cd S . . . . .           | 112.15   |
|                                                | Cd S O <sub>4</sub> : Cd O . . . . .                        | 112.35   |
|                                                | Cd : Cd O . . . . .                                         | 112.08   |
|                                                | Cd Cl <sub>2</sub> : Ag Cl . . . . .                        | 112.39   |
|                                                | Cd Br <sub>2</sub> : Ag Br . . . . .                        | 112.38   |
| 1896. Hardin . . . . .                         | Cd Cl <sub>2</sub> : Cd . . . . .                           | 112.04   |
| (Jour of Amer Chem. Soc. 18, 991.)             |                                                             |          |
|                                                | Cd Br <sub>2</sub> : Cd . . . . .                           | 112.053  |

\*Proc. Amer. Acad. Arts and Sci., 28, 200.

†Doctoral Dissertation, Johns Hopkins Univ.



In the above calculations the following atomic weights were used: oxygen 16; sulphur 32.059; carbon 12.003; chlorine 35.45; bromine 79.95; silver 107.93.

The method which we employed is in the main identical with that employed in the investigation of the atomic weight of zinc. This has been described in detail in the first part of this paper and only the points of difference will receive more than passing mention.

## II.—THE METHOD.

### *The Preparation of Pure Cadmium.*

The cadmium used was a part of that which had been prepared with great care by Dr. Metcalf and Prof. Morse in this laboratory. It was the product of the ninth distillation in a vacuum and its examination with the spectroscope showed the absence of all impurities which can be detected by this means.

Before taking the sample to be weighed, the surface of the cadmium which had been in contact with the glass was removed with a hard file, using the same precautions as were observed in the case of zinc.

### *The Preparation of the Pure Nitric Acid.*

The plan followed here is the same as that given in the first part of this paper, but the method of ascertaining its purity was more exacting. Five cubic centimeters of the acid were evaporated in a small platinum vessel, which was weighed with great care, using a similar vessel as a tare. This was three times repeated with 5 cc. portions of the acid. There was no change in the weight, nor was any visible residue formed in the vessel at the end of the test.

### *The Heating.*

In previous work the heating of the oxide was attempted in the muffle furnace; but it was found to volatilize completely at this high temperature. So Jones\* completed the decomposition of the nitrate by placing the pair of cruci-

\*Amer. Chem. J. 14, 261.

bles, 1 and 2, figure 1, page 10, in a nickel crucible and heating over a blast lamp. Later Buchert† in preparing the oxide from the oxalate, found that there was a sublimate produced in the use of nickel crucibles and substituted iron vessels.

Our first endeavor was to dispense with the use of metal vessels, and in order to reach a sufficiently high temperature, an asbestos furnace was constructed. This consisted of a larger asbestos box (cross section eight inches) open at top and bottom, which fitted snugly over a fire-brick serving for the floor of the furnace. Within this box was a smaller asbestos box, into which a No. V Berlin porcelain crucible will just pass. The large porcelain crucible is fitted into an asbestos board, which serves as a cover to the furnace when the crucible is brought into the inner box. The upper edges of both boxes were notched to admit of the escape of the products of combustion. The flames were four small blast flames, of two glass-blower lamps, which were directed into the furnace through suitable apertures cut in the asbestos boxes. The blast came from a blower, run by an electric motor, and could be regulated at the lamps, and by means of the motor. First, the proper temperature had to be determined. It was thought best to work at the highest temperature the arrangement would afford, and to try to get constant weight, examining the oxide to see if decomposition is complete, for constant weight might be gotten without complete decomposition.

As it happened the temperature employed at first gave constant weight, but later by a change in blast lamps, we attained a higher temperature and were at once impressed with the appearance of the crucibles. The white crucibles had become a yellowish brown and the lids seemed to be permeated by this color. (The glaze had been removed from the under surface of the lids. See page 10.)

Furthermore, there was clear evidence of sublimation on

†Doc. Dis. Johns Hopkins Univ., '94.

the under surface of the lids. On weighing we found a decided decrease in weight, and we were never able again with this new arrangement to reach constant weight. Two experiments gave these weights for the oxide:

|     | 1.        | 2         | 3         | 4         | 5         |
|-----|-----------|-----------|-----------|-----------|-----------|
| I.  | 1.502456, | 1.502112, | 1.502001, | 1.501628, | 1.501425. |
| II. | 1.430411, | 1.430388, | 1.430165, | 1.429923, | 1.429844. |

A determination of this temperature, which clearly produced loss of weight, fixed it between the melting point of pure silver,  $960^{\circ}$  and the melting point of potassium sulphate,  $1066^{\circ}$ , (Heycock and Neville): We turned back, therefore, to the lamps first employed, and found that they gave a temperature between the fusing point of sodium chloride and potassium carbonate,  $775^{\circ}$ - $838^{\circ}$  (Carnelley). It appeared best not to push the temperature any closer to that which produced volatilization. Having once found the adjustment of gas and blast which gave constant weight, the conditions were maintained throughout the work. That the temperature was very constant is shown by the fact that repeated tests never found it to be without the narrow limits already mentioned, e. i., between the fusing point of sodium chloride and potassium carbonate.

It required a prolonged heating in order to secure a satisfactory constant weight of the oxide. In no case was a specimen of the oxide heated less than twenty five hours, and often they were heated fifteen hours before the steady diminution in weight could no longer be noted. We adopted the rule of accepting as final the three weights whose total difference did not exceed one twenty-fifth of a milligram. From these weights we calculated the "uncorrected" atomic weight of cadmium given in the table.

It seems that Jones encountered this difficulty, for he says, "I have found that this could only be accomplished by long-continued heating."\* He refers to the decomposition of cadmium nitrate.

\*Doctoral Dissertation, Johns Hopkins Univ., 1892, page 11.

*Weighing.*

The method of weighing which was resorted to in the work on zinc commended itself for this work.

The sensibility of the balance was increased to about 6.5 divisions for 1 milligram and the weights were again carefully examined, using one of the platinum pieces as a standard. This served as a check on the values determined last year.

The weights were all corrected for air displacement.

The cadmium oxide when ready for the final test is very black, showing sometimes a little brown around edges or in patches under the lid of the crucible. It is not compact, but appears as a loose, porous, fluffy mass.

*The Determination and Analysis of the Gases.*

The apparatus presented on page 16 was used to test the oxide for gases exactly as described on page 19. It was found necessary, however, to turn the small inner crucible on its side, because of the rapid evolution of the gas when the acid came in contact with the oxide. The acid could thus flow into the outer crucible and rise slowly until it just reaches the oxide. Cadmium oxide dissolves in sulphuric acid in the cold much more readily than zinc oxide, a 36 per cent. acid dissolving it within an hour. Blank experiments were carried through with results which confirm the efficiency and accuracy of the apparatus.

When the acid was brought in contact with the oxide which had remained in a vacuum thirty-six hours, a vigorous action was set up, and bubbles of gas could be seen passing rapidly from the acid into the vacuum. It appears, therefore, that cadmium oxide derived from the nitrate under the conditions of our work retains gases. The absence of it from the oxide examined by Richards and Rogers\* is probably due to their having employed higher temperatures in their preparation of the oxide.

The phenomenon is quite different from that met with in

\*Proc. Amer. Acad. of Arts and Sci., 28, 200.



the case of zinc oxide. There we could see the gas passing off slowly and continuously as the solution of the oxide progressed; in the case of the cadmium oxide, on the other hand, the moment the acid touches the edge of the oxide (the crucible is turned on the side), a sudden drop of the mercury column occurs, a rapid condensation of moisture takes place in the vacuum and a dense fog appearing and settling leaves the surface of the mercury as if frosted. Within less than a minute almost all of the gas can be collected; not quite all, however, for as the solution proceeds one can see small bubbles of gas passing off, but this is a small proportion of the whole. The appearance gives one the impression that nearly the whole of the gas is released before the solution begins, so sudden is the escape.

After collecting the gas it was accurately measured and analyzed according to the plan outlined on a previous page. The residual gases were preserved for spectroscopic examination.

We found by analysis that the percentage of oxygen came surprisingly close to that of air.

As a test of the accuracy of our gas analytical work, we analyzed three samples of air in the same apparatus. These gave 20.79 per cent., 20.98 per cent., and 20.8 per cent. for oxygen, which we considered a striking proof of the accuracy of our method, for even the small volumes we must deal with. The volumes of air employed for the purpose were 0.371 cc., 0.510 cc., and 0.452 cc.

### III.—THE TEST FOR OXIDES OF NITROGEN.

To within recent years no attempt has been made to determine the temperature at which nitric oxide ( $\text{NO}$ ) is completely dissociated. Since the work of Berthelot, chemists have generally accepted his statements that all the oxides of nitrogen are decomposed at a dull red heat. Marignac had insisted that a frequent error of the oxide method, which employs the nitrate, must be referred to the retention of undecomposed oxides of nitrogen. Morse and

Burton\* have shown that this error did not apply to their work on zinc. More recently, Jones† and Bucher‡ have examined cadmium oxide with similar results. Since their work Emich|| attempted to fix the dissociation temperature of nitric oxide by passing the gas through heated tubes and examining it with oxygen and iron sulphate solution. He found very slight dissociation at 700°, very little more at 900°, about two-thirds at 1,200°, and not complete dissociation till the melting point of platinum is reached.

C. Langer and Victor Meyer§ in 1888 state that nitric oxide is not at all dissociated at 900.-1200°, but is completely decomposed at 1,690°. The gas was passed through heated tubes and examined with pyrogallic acid.

Nevertheless, it was considered very important to submit this question of the presence of oxides of nitrogen in the oxide once more to a rigid test. Not being able to apply the method employed by Morse and Burton and by Jones and Bucher to our oxides, the following plan was pursued: two samples were sacrificed to make doubly sure of the test. These were brought into wide-mouthed bottles which were immediately closed on introducing the sulphuric acid. It is evident that if oxides of nitrogen were present, nitric acid must be formed, because of the free oxygen and water present, and the latter can be tested for in the sulphuric acid and in the washings of the bottle. The same result must follow when we dissolve the oxides in the vacuum, *if free oxygen is present*, and the acid used in the solution can be tested for nitric acid.

The test for nitric acid which commended itself was the brucine test, its only fault being its too great delicacy, since it is difficult to prepare a sulphuric acid that will not give a slight color reaction with brucine. The purest sulphuric acid was used for the solution of the oxides and a fresh sample of this same acid was used for making the test. The brucine was an unusually pure specimen. Two porce-

\*Amer. Chem. J. 10, 321.

†Amer. Chem. J. 14, 261.

‡Doctoral Dis. J. H. U., page 21.

||Monatshefte f. Chem. 13, 615, 1892.

§Pyrochemische Untersuchungen, page 66.

lain lids were used for the test. Twenty drops of the pure concentrated sulphuric acid were brought on each lid and equivalent quantities of brucine were stirred into the acid. There was a faint tinge of color noticed in both solutions. A drop of the sulphuric acid prepared for dissolving the oxide was drawn through the solution—on one lid—and simultaneously a drop from the crucible just removed from the vacuum was drawn through the other, a faintly visible streak of color is left in each solution, but no difference in the distinctness of the colors could be detected. For the purpose of a comparison a drop of a nitric acid solution prepared to contain 1 part in between 20,000 and 30,000 was drawn through one while a drop from a nitric acid solution containing 1 part in between 70,000 and 80,000 was drawn through the other. In the former case, the color pervaded the whole solution; in the second, a very strong rose purple streak was developed, which was many times more distinct than that produced by the drop of acid which had dissolved the oxide.

There was, therefore, no nitric acid present in the acid which dissolved the oxides in the closed bottles, nor was any found in the acid used in the solution of the nine samples of oxide recorded in the table on a following page. Furthermore, the gas obtained from two experiments was tested with pure oxygen. When oxygen was introduced into the eudiometer, there was no color and no change of volume. Finally, analysis showed that about one-fifth of the gases is pure oxygen, so the test for nitric acid described above remains valid and conclusive. We are in a position to confirm the statements of previous investigators, that oxides of nitrogen are not present in cadmium oxide prepared in this way.

#### IV.—THE TEST FOR NITRIDES.

The acid which had dissolved the various samples of the oxide was carefully preserved and the amount of ammonia present in it was determined by Nessler's reagent. The quantity was found to be very small and not greater than

that found in the original sulphuric acid. There appear, therefore, to be no nitrides formed in the preparation of the oxide.

#### V.—THE SPECTROSCOPIC EXAMINATION OF THE RESIDUAL GASES.

The gases were prepared for examination precisely as described in the first part of this paper.

The spectroscopic work was under the supervision of Prof. Ames, of the Physical Laboratory.

He reports that there was abundant evidence of nitrogen and a few lines indicating oxygen, but no other gas could be detected. There was no evidence whatever of carbon dioxide or argon. In the presence of large quantities of nitrogen, however, it is possible for very small quantities of these gases to escape notice. The oxygen, of course, was introduced in preparing the gases for the sparking tubes.

#### VI—RESULTS.

Below the results of the work are given in tabular form. Nine experiments were carried through, after the preliminary testing, to determine the proper temperature and to prove the absence of oxides of nitrogen, had been completed. (In order to be very sure that oxides of nitrogen were not present in the specimens of oxide used in these nine experiments, the acid, which had dissolved the oxide, was at the end of each experiment tested for nitric acid as above described.)

The results of three blank experiments are included.

The vacuum weights of the cadmium and the cadmium oxide are given, the atomic weight of oxygen is taken as 16 in the calculations, and the gas volumes are given under standard conditions.

## SUMMARY OF RESULTS.

| Number of<br>Samples | Weight<br>of<br>Cadmium | Weight<br>of<br>Oxide. | Uncor-<br>rected<br>Atomic<br>Weight. | Gas<br>Volume<br>0°, 760 mm. | Percent-<br>age of<br>Oxygen. | Corrected<br>Atomic<br>Weight. |
|----------------------|-------------------------|------------------------|---------------------------------------|------------------------------|-------------------------------|--------------------------------|
| I                    | 1.931882                | 2.207639               | 112.092                               | 0.574 cc.                    | 21.25%                        | 112.392                        |
| II                   | 1.679348                | 1.919096               | 112.074                               | 0.480 cc.                    | 25.16%                        | 112.365                        |
| III                  | 1.484296                | 1.696195               | 112.076                               | 0.441 cc.                    | 19.95%                        | 112.376                        |
| IV                   | 1.364861                | 1.559717               | 112.071                               | 0.402 cc.                    | 18.33%                        | 112.368                        |
| V                    | 1.502948                | 1.717441               | 112.112                               | 0.419 cc.                    | 21.95%                        | 112.394                        |
| VI                   | 1.438035                | 1.648297               | 112.093                               | 0.431 cc.                    | 18.56%                        | 112.395                        |
| VII                  | 1.440410                | 1.646087               | 112.079                               | 0.406 cc.                    | 20.93%                        | 112.365                        |
| VIII                 | 1.459384                | 1.667714               | 112.082                               | 0.421 cc.                    | 21.85%                        | 112.375                        |
| IX                   | 1.403791                | 1.604196               | 112.076                               | 0.390 cc.                    | 19.50%                        | 112.359                        |
| Mean=112.084         |                         |                        | Mean=112.377                          |                              |                               |                                |
| Max. dif. from Mean= |                         |                        | Max. dif. from Mean=                  |                              |                               |                                |
| Total Difference=    |                         |                        | Total Difference=                     |                              |                               |                                |

## BLANK EXPERIMENTS.

|     |                                                         |
|-----|---------------------------------------------------------|
| I   | 0 cc.                                                   |
| II  | 0 cc.                                                   |
| III | 2 mm=(less than .01 of a cc. at<br>standard conditions. |

## VII —REMARKS.

The uncorrected atomic weight figure 112.084 agrees very closely with that of Morse and Jones, 112.07, and is almost identical with the average of Bucher's two experiments, using porcelain vessels, 112.08. Our work explains the necessity of long continued heating to get a so-called "constant weight" of the oxides.

Apparently small quantities of gases are driven off for a long time, before at a given temperature no further decrease in weight can be detected by the balance. It still remains doubtful whether or not the same weights would be found, if the oxides could be heated for a very long time, say several hundred hours. In this case the uncorrected atomic weight figure might be higher and the quantity of gas abstracted proportionately small.

It is of interest to note the very constant volumes of gas per gram of the oxide:



|               |                |               |                 |
|---------------|----------------|---------------|-----------------|
| I. 0.260 cc.  | III. 0.260 cc. | V. 0.244 cc.  | VII. 0.246 cc.  |
| II. 0.250 cc. | IV. 0.258 cc.  | VI. 0.262 cc. | VIII. 0.252 cc. |
|               |                |               | IX. 0.243 cc.   |

The mean is 0.253 c. c., which is less than that of zinc oxide, 0.301 c. c.

There are striking differences between the oxide of zinc and the oxide of cadmium in respect to the phenomena which are observed when the gases in them are liberated by an acid. In the former case the gases were given off slowly as the oxide dissolved, some persisting to the very last; in the latter case we find the gases given off suddenly and nearly the whole amount immediately. Again, we found widely different percentages of oxygen in the one instance, while in the other there is a uniformity in this respect.

The acid bulb of the apparatus was carefully washed and a neutral water was introduced and when exhausted it was brought into contact with the oxide in the vacuum. No effect whatever was produced by the water. Though remaining soaked with water for three days, the oxide yielded not a trace of gas. When a few drops of a weak acid, however, were added, the gases were given off as before very suddenly. It is, therefore, evident that the gas is not liberated when the oxide is submerged in water in a vacuum.

An experiment was also made to determine whether the gas can be liberated on heating the oxide under water.

A specimen of oxide was prepared with the same care that was exercised in the previous experiments and was then treated with water and boiled for six hours. The oxide was thus broken up into a very fine powder. As soon as it had cooled for a few minutes, the crucibles containing it, covered with the water in which it had been boiled, were brought into the apparatus, page 16. When the exhaustion was complete, the acid was allowed to pass into the crucibles and immediately gas was liberated. The volume per gram was not noticeably different from that found in

our regular determination and the attending phenomena were very similar.

In view of the facts presented, it is clear that further investigation will be required to furnish any definite conclusion as to the way in which these gases are held in the metallic oxides. That cadmium oxide presents an especially interesting problem, can no longer remain in doubt. Our work has demonstrated the fact that cadmium oxide, derived from the nitrate by heating to a temperature not more than two hundred degrees below the temperature of initial volatilization, retains gas, a fact hitherto unknown.

That Richards and Rogers obtained no gas from cadmium oxide is probably explained by their having heated their oxide to a much higher temperature than we were able to heat ours on account of volatilization of the oxide at temperatures between  $960^{\circ}$  and  $1066^{\circ}$ . The exact temperature of beginning volatilization requires further investigation.

It might be expected that the preliminary samples which had been heated too high would give a smaller amount of gases, but the difference is too slight to afford any definite information. It must be borne in mind, however, that these were heated not more than two hundred degrees higher than those of the regular determinations and the volatilization had just begun.

There seem to be no constant errors in this method, but as a chief disadvantage the small difference in weight of the cadmium and cadmium oxide, whereby the necessary errors of weighing are multiplied, must be named, while the possible errors of measuring and analyzing the gases play a small part. Even if these errors were cumulative, which is not at all likely, the true figures will be very slightly removed from the mean of those given.

#### VIII.—THE ATOMIC WEIGHT OF CADMIUM.

The figure 112.377 is very near the figure 112.39, obtained by Bucher,\* by determining the relation of cad-

\*Doc. Dis. Johns Hopkins University, 1894.

mium chloride to silver chloride, and is practically identical with the figures 112.38, obtained by him in his investigation of cadmium bromide. Bucher's individual experiments show an unusually large difference because of the many variations of his method. His lowest determination is 112.28, while his highest reaches 112.48. It also lies within the limit of Dumas' results by the halogen method, 112.007-112.476. It differs from the results of Huntington and Cooke by 0.13 and 0.14 respectively, which is no greater than the difference between the highest and lowest determinations in their two series.

The problematical average, 112.325, of the best results by the halogen method thus far differs from our figure by only 0.054. The direct oxide method can no longer confirm the lower results of the oxalate, sulphide and electrolytic methods, which are not without special sources of error, and the facts brought to light in this work point to a higher atomic weight figure for cadmium than that generally accepted, 111.95. We incline to the opinion that 112.4 must be a close approximation to the truth.

In conclusion, we cannot refrain from expressing the hope that Richards will bring his highly perfected bromide method, which has given such signal success in other cases, to bear on the cadmium problem.

BIOGRAPHICAL SKETCH.

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HOWARD BELL ARBUCKLE was born on October 5, 1870, near Lewisburg, W. Va., Greenbrier county.

He received his early education in the public schools of that county, going in the fall of 1884 to Prince Edward Academy in Virginia, and entering Hampden-Sidney College the next year. He was graduated in June, 1889, with the degree of Bachelor of Arts, and was appointed Fellow and instructor in the college for the ensuing year.

In the following June, 1890, the Master of Arts degree was conferred upon him.

The five years immediately succeeding this were spent in teaching, one year in a Normal College in northern Mississippi, and four years as instructor in Natural Sciences in the State Seminary west of the Suwannee at Tallahassee, Florida. During this time he spent two summer sessions at the University of Virginia studying Chemistry under Prof. J. W. Mallet.

In 1895 he entered Johns Hopkins University as a graduate student, and has since been pursuing advanced courses in Chemistry, Physiology and Biology. In 1898 he was appointed University scholar in Chemistry.







